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VI.

On a Process of Fractional Condensation; applicable to the Separation of Bodies having small Differences between their Boiling-Points.

BY C. M. WARREN.

Communicated May 10th, 1864.

It is well known that the process in general use for the proximate analysis of mixtures of volatile liquids, — viz., that of simple fractional distillation, either from a tubulated retort or from a flask with bulbs, as proposed by Wurtz,* — affords but very imperfect and unsatisfactory results, and not unfrequently leads to gross errors and misconceptions, except in those cases in which the boiling-points of the constituents are widely different, or in which some auxiliary method can be advantageously employed.

The want of a more efficient process for effecting such separations has long been recognized. There are numerous natural and artificial products, of the highest scientific interest, — such as petroleums, essential oils, tars, and other mixtures of oils obtained by the distillation, under varied circumstances, of bituminous, vegetable, and animal substances, — of which it may at least be said that we have but very imperfect knowledge, — I might almost say no knowledge, except such as could be derived from the study of very impure materials, — still mixtures of different bodies, — with which, instead of the pure substances sought for, chemists have felt compelled to content themselves, as the best results which they were able to obtain by the means at their command.

In repeated instances, apparently after persevering and protracted efforts, investigators have been forced to assert either the impossibility, or their inability, to obtain, from such mixtures, bodies of constant boiling-point, — a property which is generally received as a test of purity for liquid bodies.

I may here specify a few recent instances of this kind.

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* Annales de Chimie et de Physique, 3e Série, XLII. 132.

1. Warren de la Rue and Hugo Müller,[*] in their paper entitled "Chemical Examination of Burmese Naphtha or Rangoon Tar," after detailing the preliminary treatment by distillation in a current of steam, add that "A further separation of the various products was effected by repeated fractional distillations; but no absolutely constant boiling-points could be obtained, notwithstanding the great number of distillations and the large quantity of material at command. It is true that considerable portions of distillates could be collected between certain ranges of temperature, tending to indicate a constant boiling-point; nevertheless it soon became evident that distillation alone could not effect the separations of the various constituents, and that recourse must be had to other processes." The other processes resorted to were, treatment with sulphuric and nitric acids, either separately or mixed; but still with very imperfect results. This acid treatment, which was first proposed by De la Rue, and subsequently employed by C. Greville Williams,[†] Schorlemmer, and others, will be further noticed below.

2. Frankland,[‡] in speaking of a mixture of the hydrocarbons of the formulæ $C_n H_n$ and $C_n H_{n+1}$ (now generally considered as $C_n H_{n+2}$), which have a difference of 6° to 7° C. between their boiling-points, says, "The separation of two such bodies by distillation alone is impossible"; and suggests that the employment of anhydrous sulphuric acid may accomplish the object by dissolving out the body of the formula $C_n H_n$.

3. And so recently as 1862, Schorlemmer,[§] in his first paper "On the Hydrides of the Alcohol-Radicals existing in the Products of the Destructive Distillation of Cannel Coal," remarks that "it was, however, found impossible to obtain a product of constant boiling-point by repeated fractional distillations"; and he also had recourse to the acid-treatment above referred to.

4. Pebal,[‖] after an elaborate research on the petroleum from Galicia, in which Wurtz's bulbs were employed, and also Eisenstuck,[¶] who made an extended investiga-

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[*] Proceedings of the Royal Society, VIII. 221.

[†] Philosophical Transactions, 1857, 447.

[‡] Quarterly Journal of the Chemical Society, 1851, 3, 43.

[§] Journal of the Chemical Society, XV. 419.

[‖] Annalen der Chemie und Pharmacie, CXV. 20, asserts the "Unmöglichkeit, das Gemenge durch fractionirte Destillationen zu entwirren."

[¶] Annalen der Chemie und Pharmacie, CXIII. 169, says as follows:—"Mit den 5° zu 5° aufgesammelten Destillaten wurde die fractionirte Destillation wieder von Neuem vorgenommen, aber nachdem diese Operation sieben Wochen mit etwas 50 Pfund Steinöl fortgesetzt worden war, erhielt ich doch kein Product von irgend constantem Siedepunkt. Nach diesen Versuchen halte ich es für Unmöglich, das Steinöl durch fractionirte Destillationen allein in Producte mit constantem Siedepunkt, zu scheiden."

tion of the petroleum from Sehnde, near Hannover, also with the use of Wurtz's bulbs, both assert in the most positive manner the impossibility of separating from petroleum, by fractional distillation, products of constant boiling-point.

Such is the general character of the results obtained in the attempts which have been made to separate the constituents of such mixtures by fractional distillation.

The treatment with strong acids, etc., as an auxiliary to the common method of fractional distillation, which is claimed to have given good results in some cases, is open to serious objections in its application to mixtures of unknown substances, as must be readily apparent. The further consideration of this subject is reserved for another occasion, when I shall submit the results which I have obtained by my process in the study of mixtures almost identical with some of those in the investigation of which the acid process has been employed. I shall then be able to show that the results obtained by that process are, to a considerable extent, inaccurate and by no means exhaustive; and that it is still of the highest importance to have a process which shall be generally applicable in all such cases, without resort to any harsh and uncertain treatment.

With regard to the value of constancy of boiling-point above referred to, as a test of purity of a liquid substance, I may here say that, without scarcely lessening the importance of obtaining constancy of boiling-point, before resorting to harsher treatment, in the study of mixtures of unknown substances, I think I shall be able to show, on another occasion, that this property is not necessarily indicative of so high a degree of purity as has generally been supposed; and that a body may have a constant boiling-point, and yet contain enough of a foreign substance to appreciably — and, in delicate cases, seriously — affect the determination of its constitution and of some of its other properties. But in no such case have I yet found that the removal of the impurity by chemical means has essentially changed the boiling-point, — *i. e.*, never to the extent of 1° C. of temperature. I propose, at a future time, to study this question synthetically, operating with pure liquid substances, with the view to determine, in a few cases, how much of a foreign substance may be present, — which would probably be variable in different cases, — without sensibly affecting the boiling-point. A solution of this question would, I think, be of considerable practical value in some instances.*

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* Since this was prepared for the press I notice that late experiments by Berthelot go to show the correctness of my conception of the value of constancy of boiling-point, as above stated.

Of the New Process.

The chief distinctive feature of my process, as compared with the common one, consists in this, — that the operator has complete and easy control of the temperature of the vapors given off in distillation; and consequently can readily cool these vapors to the lowest limit of temperature which the most volatile portion, under the circumstances, is able to bear and retain its vaporous condition. It will be seen at a glance that, under these conditions, the operator has it in his power to secure in any case the very largest possible amount of condensation of the heavier from the lighter vapors. The liquids resulting from the condensation of the less volatile portions of course fall back into the retort, while the vapors of the more volatile parts continue to go forward to a cold condenser, descending in the opposite direction, from which the condensed product falls into a special receiver. In this manner he is able to obtain, in each successive operation, a series of products which shall contain the minimum quantity of the less volatile constituents, which a single distillation is capable of affording.

Of the common process, on the contrary, nearly the reverse of all this is true: the operator having no control whatever; being forced to receive the vapors at the temperature which they naturally acquire in passing from the retort, and laden with such proportion of the less volatile bodies as may be carried forward with them.*

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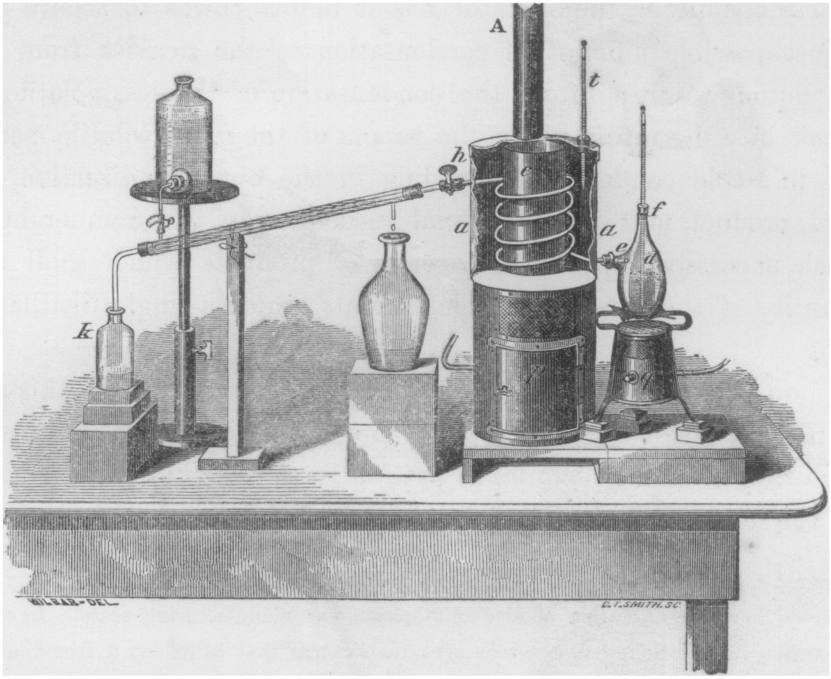
* The only apparatus, of which I have any knowledge, which can be regarded as bearing any analogy to my own, is that employed in the rectification of alcoholic spirits, on a manufacturing scale. In one of the older forms of this apparatus, that of Solimani, to which my attention was first called by a friend, after my process had been in use more than a twelvemonth, the temperature of a dephlegmator is kept within such limits as to give alcohol of any required strength more readily than by the common methods. The mode of construction of this apparatus is, however, only adapted to manufacturing purposes, and it could not be utilized in the more exact experiments required in scientific research. Either on account of its complication, or some other cause, the apparatus of Solimani has, I believe, long since been abandoned.

Mansfield (Quarterly Journal of the Chemical Society, 1849, I. 264), observing that "the boiling-point of benzole is the same as that of alcohol of sp. gr. 0.825," remarks that "any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits, are applicable to the separation of benzole from the less volatile fluids of naphtha"; and, appended to his scientific treatise on coal-tar, under the title "*Of a Practical Mode of Preparing Benzole*," goes on to describe a process for that purpose, which I believe, he had previously patented. It appears that Mansfield did not employ this process in his research, but obtained his benzole, as well as the other less volatile hydrocarbons, in the usual manner, — by simple distillation.

In the belief that no process of fractioning at all analogous to mine has ever been employed in scientific research, and that I am not in any way directly indebted to any of the devices of my predecessors, I have taken no special pains to consider these devices in much detail. I may say, however, that I have found no

In the new process, perfect control of the temperature of the vapors is secured by simply conducting these vapors upward through a worm contained in a bath, *aa*, Figs. 1 and 2, the temperature of which is regulated by means of a separate lamp, *b*, Fig. 2, or by a safety-furnace, *p*, as shown in Fig. 1. The bath may be of oil or water, or of metal for very high temperatures, as the case may require, and is furnished with a thermometer, *t*.

Fig. 1.



That this bath may be equally adapted for the separation of liquids boiling below the common temperature, an empty vessel, *c*, Fig. 1 and 2, is permanently secured in the interior of the bath by means of straps of metal across the top, to serve as a convenient receptacle for ice or iced water, by means of which a low temperature may be steadily maintained. This interior vessel also serves a good purpose in economizing

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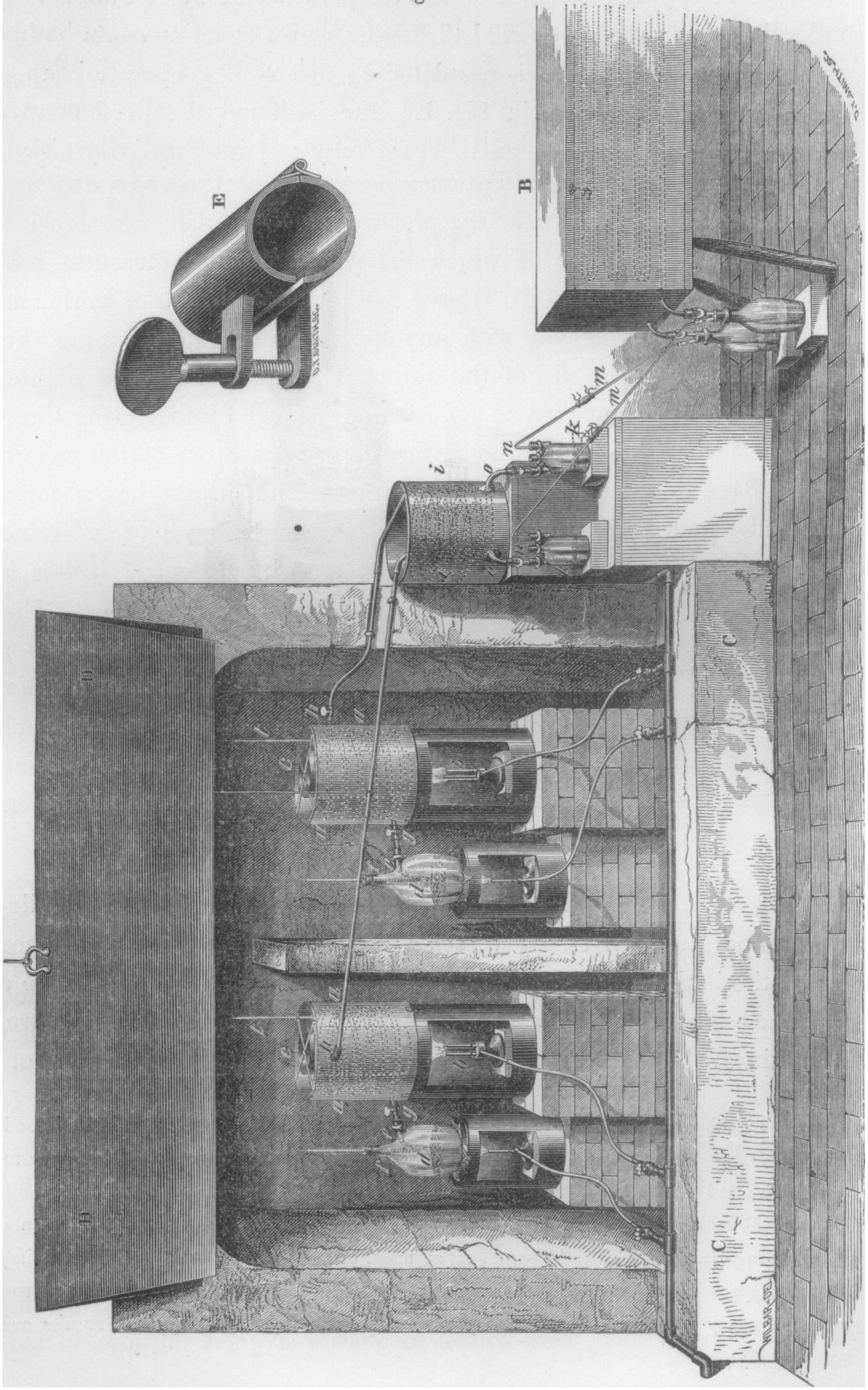
record of any one's ever having employed the oil bath and a separate fire to regulate a heated condenser, this being the essential feature on which the superiority of my process is based; adapting it at once to both high and low temperatures, and for the most delicate work.

The employment of bulbs, above referred to, as proposed by Wurtz, is simply a modification of the old process. The bulb apparatus furnishes the same, or, at most, but slightly better results than a simple retort; being no more than equivalent to increasing the height of the sides of the retort itself, without introducing any control over the accuracy of the results; the only advantage gained being, that these results are obtained somewhat more quickly.

Fig. 2.



time, and fuel in heating the bath, as it diminishes the quantity of oil required to cover the worm. It is made to extend to within about three inches of the bottom of the bath, and large enough to fill the greater part of the space in the centre of the coil. The bath and interior vessel are both made of sheet-copper, with joints brazed so that they will bear a high temperature. I generally use, also, copper worms, especially in the earlier distillations, the quantities then operated upon being larger, as such worms are conveniently procured, and not liable to break. In the larger-sized apparatus, the tube of which the worm is made measures ten feet in length and half an inch in diameter. I have tried several lengths of worm and several diameters of tube, but not, as yet, with any special view of determining the precise proportions, in relation to the size of the retort, which would be best adapted to the purpose. There appears, however, to be nothing gained by increasing the length of the worm beyond what is required to reduce the temperature of the vapors to that of the bath. I have in use three sizes of apparatus: the largest has a copper worm 10 feet long and $\frac{1}{2}$ inch bore; the medium size, a worm 5 feet long and $\frac{3}{8}$ inch bore; and the smallest size, for very small quantities, a worm 1 foot 6 inches long and $\frac{1}{4}$ inch bore. Each of these has been found to answer a good purpose. The distillation may be conducted in a glass flask, or more conveniently in a glass retort of the form shown at *d*, Fig. 1 and 2. The body of this retort, as appears in the figure, is of the form of the corresponding part of the common retort; but which, in place of a long neck, has only a short tubulure, *e*, in the side, for escape the vapors, and another tubulure, *f*, in the top, which contains the thermometer, and through which the retort is charged.

In the larger apparatus the retort is connected with the lower end of the elevated worm by means of a glass tube of about the same diameter as the end of the worm. One end of this tube enters the retort at the lateral tubulure through a perforated cork, and the other end is joined to the end of the worm either by being firmly bound with a strip of cloth thickly covered with vulcanized caoutchouc, — such as is found in commerce, — or by means of a perforated cork, which is made to fit the ends of both tubes as snugly as possible, and then tightly pressed together upon the joint by means of an iron clamp, as shown at *g*, Fig. 2. This clamp is figured on a larger scale at E. As it is highly important that all joints in the apparatus should be perfectly tight, inasmuch as the least leakage, when continued a long time, would cause, in the aggregate, a serious loss of material, I would call special attention to the clamp joint as the best which I have tried. Before falling upon this device I had used exclusively the vulcanized caoutchouc joints, which were found to answer a good purpose, in most cases, except that they required too frequent renewal. I have found the cloth covered with vulcanized caoutchouc preferable to the common caoutchouc tubing. In the smaller sizes of apparatus I have the end of the worm itself project far enough from the bath to connect directly with the retort by means of a perforated cork, without the use of an additional connecting tube.

The upper end, *h*, of the elevated worm is brought out through the side of the bath at a point about three inches below the top; so that, when working with a low temperature of the bath, the worm may still be completely covered with oil, and also give sufficient space above the worm for the expansion of the oil when higher temperatures are employed. To avoid contaminating the atmosphere of the laboratory with the disagreeable fumes which are given off, in large quantity, from such a mass of heated oil, the top of the bath is tightly closed with a sheet-iron cover, from which a small funnel, A, Fig. 1, conducts these fumes to a chimney.

In the larger apparatus, the vapors which succeed in passing through the heated worm are conducted downward into a cooled worm contained in a bath of water, *ii*, Fig. 2, and the liquid product is collected in the receiver, *k*. The cold bath, *ii*, contains two condensing worms, — one for each apparatus, — and is large enough to condense for both without the necessity of renewing the water. I have represented two apparatuses combined, as it will be found more economical of time to operate with two at once. In the smaller apparatus, for the table, a Liebig condenser may be conveniently substituted for the cold worm, as shown in Fig. 1.

For collecting liquids which boil below the common temperature, when such are present, I attach a refrigerator, B, Fig. 2, which is provided with two block-tin condensing-tubes, — one for each apparatus. These are bent in a zigzag form, and attached to the inner sides of the refrigerator. The lower ends of the tubes extend through the end of the refrigerator far enough to form a convenient connection with the second receiver, *l*, Fig. 2, which communicates with the first receiver, *k*, by means of the glass tube, *m*.

In order to successfully collect and condense the vapors of such extremely volatile liquids as are now under consideration, it is of course indispensable that the apparatus should be constructed with very tight joints; and for greater convenience, but more especially to prevent breakage, such of the joints as require to be frequently taken apart should be made flexible. A very convenient and perfectly tight joint of this kind may be made as follows: — the short stationary tube, *n*, in the cork of the receiver, *k*, Fig. 2, is made with the opening somewhat divergent upward; the end, *o*, of the worm is enough smaller than the inside diameter of the upper end of the tube, *n*, to leave room for a piece of caoutchouc tube to be drawn over it, and still admit of its being inserted in the end of the tube, *n*; the flexible tube is drawn on far enough to prevent the drops which form on the end of the worm from coming in contact with the caoutchouc; a perfectly tight and convenient flexible joint is now made by pressing the tube, *n*, over the caoutchouc covering of the end of the worm, *o*. The joints of the receivers, *ll*, are made in the same manner.

The vapors which escape condensation in *ii* pass through the receivers, *kk* and *ll*, to the refrigerator B, which contains ice, or a mixture of ice and salt, are there condensed and fall back into the receivers, *ll*; which should stand in a wooden vessel also containing ice or a freezing mixture. The refrigerator, B, is made with double bottom and sides, with an inch space between, which is filled with pulverized charcoal. Being tightly covered, a charge of ice and salt will serve for a long day's operations without renewal. In this manner I have been able to collect, in considerable quantity, bodies boiling nearly at 0° C., and this from mixtures in which such bodies had been quite overlooked by previous investigators.

It will be observed, on reference to Fig. 2, that the larger distilling apparatus is represented as standing in a brick fire-place, with brick-work, CC, a few inches high, built up in front; and a sheet-iron apron, DD, folded above. This is for security against fire in case of accident, either to the retort or hot bath of oil. As arranged, the contents of either or both of these could run out and burn without danger to the operator or the premises, as the brick-work in front would prevent the liquid from spreading beyond the fire-place, and the dropping of the sheet-iron apron would cause an additional draft, and thus insure the passage of the flames into the chimney. Instead of placing the apparatus in a fire-place, where that is not convenient, equal security against accidents may be attained by the use of my safety heating-lamp,* *q*, Fig. 1, to heat the retort, and safety-furnace, *p*, containing a Bunsen's burner, for heating the bath. The bottom of this furnace, and also a large part of the sides, is formed of wire gauze, such as described for the safety-lamp.† The gauze upon the bottom need not be permanently attached to the furnace, but may be simply laid over an opening cut in the stool or board on which the furnace is to be placed; if the furnace be then set upon it, taking care that the joint shall be tight around the edge, nothing more will be required. A strip of vulcanized caoutchouc, about an eighth of an inch in thickness, is riveted around the edge of the opening for the door; against this the door tightly closes, so that no ignition can take place through the cracks which would otherwise remain under the edges of the door.

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* American Journal of Science, 1862 (2), XXXIII. 275.

† *Loc. cit.*

For an apparatus to stand upon the table, the safety-lamp and furnace are especially desirable. I have also used them for the larger apparatus, placed upon the floor of the laboratory. As a practical test of the security which they afford, I may relate an incident which happened to myself. I had left the laboratory for a short time, with such an apparatus in full operation; the retort containing nearly a quart of light petroleum boiling below 100° C. Having been detained longer than I expected, on returning I found the laboratory filled with the vapors of hydrocarbons; and, on approaching the retort, found that the caoutchouc joint, connecting the retort with the elevated worm, had failed, and that the larger portion of the liquid had distilled into the room, having been mainly condensed in the upper worm, and conducted thence down the outside of the retort into the safety-lamp. This process was still going on, the lamp being highly-heated from the excess of fuel thus added to it, but no ignition took place outside the lamp. Although this experiment was rather injudicious, it furnishes a valuable test of the efficiency of the safety-lamp and furnace.

Having described the apparatus, I now proceed to give such details of the method of conducting the separations as have been found, in my experience, most efficient and economical of time. In commencing with a crude mixture of unknown liquids, I deem it advisable to operate at once on a tolerably large quantity of material, especially if the constituents are supposed to be numerous, and to omit chemical treatment till after the separations have so far progressed as to indicate the number and species of bodies present, and, approximately, their several boiling-points.

Notwithstanding the precautions taken to avoid loss from evaporation and leakage, I have at times been surprised at the large waste of material which has been made apparent after a long series of operations. When it is considered, however, that the time required to make a complete separation of a very complex mixture of liquids must necessarily be very protracted, during which more or less of evaporation is constantly taking place, it will be a matter of no surprise that the loss is so considerable. The quantity of material required must depend also on the proportions in which the various constituents are contained in the crude mixture, and upon their degree of volatility; but as these cannot be known *a priori*, it may suffice to make a single preliminary distillation of a portion of the mixture, from a tubulated retort, to ascertain the range of temperature within which it distills, noting at the same time the proportions which come over between certain temperatures; as, for example, below 50° C.; between 50° and 100°, etc.; from these data one may judge pretty nearly of the quantity which it will be advisable to take. It is evident that, when very volatile bodies are present, even in considerable proportion, a much larger quantity would be required than if the material were but slightly volatile; as the waste in the former case, from evaporation, would be much greater.

But in many cases it will be found that highly volatile bodies are present only in very small proportion, — e. g. in viscid petroleums like Rangoon tar, and in the products of distillation of some species of asphalt. In such cases, the requisite quantity to be operated upon, to obtain the most volatile constituents in sufficient quantity for anything like a complete study of their chemical relations, would be extremely large, — too large to be conducted in the laboratory, — and one would have to resort to the manufactory for the first distillation. I have dwelt at some length on this point, having experienced the disappointment which one feels, after months of labor, on finding the products insufficient for his requirements, when the expenditure of a little more time, comparatively, might have given double the quantities obtained.

In the first series of fractioning I generally operate on successive portions, of about one gallon each, of the crude material, and take off a fraction for every 20° C. rise of temperature of the retort. These fractions are preserved in well-stoppered bottles, and each carefully labelled with the temperatures between which it was obtained. The fractions for each fresh portion of the crude material, being collected between the same limits of temperature, are added to the corresponding products from the preceding operations, till enough of the crude material has been taken to insure, ultimately, a sufficiency of the pure products.

In the commencement, not only of this but of all subsequent fractionings, when the temperature to which the bath should be raised is unknown, I first bring the liquid in the retort into full ebullition, so that a steady stream of liquid shall flow back from the end of the worm into the retort. I then carefully raise the temperature of the bath until the vapors from the retort pass through the heated worm so freely that the liquid, in condensing from them, shall drop with tolerable rapidity into the cold receiver. In order that this dropping may be continuous, it is necessary that the temperature of the bath should rise *very gradually* as the more volatile constituents of the mixture are taken off; this is easily effected by carefully regulating the flame under the bath.

It is advisable to boil the retort as rapidly as possible without choking the lower end of the heated worm with the returning liquid. As this choking would give rise to additional pressure in the retort, and consequently occasion abnormal elevation of the temperature, and possibly a rush of liquid into the receiver, and thus introduce irregularities in the work, excessive heat under the retort should be avoided. The first indication of choking of the worm is a partial or entire stoppage of the stream of liquid which normally flows steadily from the end of the worm into the retort. Any interruption or unsteadiness of this flow would indicate too rapid ebullition.

As a rule, other things being equal, the greater the difference between the temperature of the bath and that of the retort, the slower the products will come off, and the more effectual will be the separation. I think it possible, however, that the earlier fractionings may be conducted so slowly that the loss of time would more than counterbalance what might be gained by more thorough separation, and that equally good results may be more economically obtained by more frequent operations, somewhat more rapidly conducted.

A striking illustration of the advantage to be gained by this process is presented by the fact that, during the first fractioning of a crude mixture, such as American petroleum or coal-tar naphtha, for example, the difference between the temperature of the bath and that of the retort may sometimes be as much as 35° C., or even more. While, as the products become purer, this difference between the temperatures of the bath and retort proportionally decreases, till finally, in operating on a pure product, the temperature of the bath must be brought to within a few degrees of that of the retort, in order to bring the vapors through. But the amount of this difference is variable for different bodies of equal purity.

These first fractionings must necessarily be quite arbitrary; for, as a general rule, when operating on such mixtures as those just mentioned, neither the thermometer nor the quantities obtained for any given range of temperature will indicate any decided preponderance of any one substance. On the contrary, the temperature rises uniformly, and about the same quantity is generally obtained for the same number of degrees of temperature throughout the operation. In other mixtures, in which certain bodies may seem to be present in much larger proportion than others, or in which there may be a greater difference between the boiling-points of the constituents than in the cases referred to, — facts which would be indicated by the thermometer of the retort, and by the relative quantities of the products obtained, — there might be something gained by exercising discretion in taking off fractions according to these indications.

In the second series of fractioning, the first or lowest fraction of the preceding series, which is large enough to operate upon by itself, is transferred to the retort, and brought into ebullition. The temperature of the bath is then adjusted as above described, and the distillation continued, the fractions obtained being placed in their appropriate bottles until the temperature of the retort shall have risen to, or somewhat above, the point at which the second or next succeeding fraction of the first series may be supposed, or has been found by experiment, to boil. This fraction is then added to the residue in the retort, and the distillation is continued as before. In the same manner, I proceed with the remaining fractions of the first series.

All subsequent fractionings are similarly conducted. As the work progresses, however, the fractions are taken for a gradually decreasing number of degrees of temperature, until finally it becomes necessary, for the attainment of absolute constancy of boiling-point, to take off a fraction for every degree, centigrade; and to continue thus to operate on these fractions, each representing one degree of temperature, until the desired end is attained.

The operator will observe that, in each series of fractions, in which each fraction has been taken for the same range of temperature, the difference between the boiling-points of any two contiguous fractions is nearly the same as the difference between any other two contiguous fractions, — in other words, that the difference referred to approximates to a common difference throughout the same series. Once ascertained, this difference serves as a valuable guide in determining with sufficient accuracy when to add the next fraction to the retort. By observing this systematic course, irregularities, from the improper mixture of products, may be avoided, and time thus economized.

After a few series of fractionings, — sometimes after two or three, variable in number, according to the nature or complication of the mixture, — it will be found that some of the fractions are considerably larger than others for the same range of temperature, indicating approximately the boiling-points of the several constituents. But fractions of constant boiling-point, or those, the boiling-points of which cannot be sensibly changed by further fractional condensation, are not obtained, as already mentioned, till after repeated careful fractioning for every degree of temperature. When fractioning for every degree, it is important to use every precaution to protect the thermometer from external influences, and to carefully apply the corrections for variations in the atmospheric pressure. This may even be desirable earlier; but it is of so much importance in the case specified, that, if omitted, the operator would be liable one day to mix products which he had separated the day previous.

In this way, certain larger fractions are obtained, which are not susceptible of further alteration in their boiling-points; but there are yet considerable quantities of liquid in the intermediate fractions, which still continue to change more or less in each succeeding operation. When the fractions of constant boiling-point have once been obtained, if it were not important to test for other bodies in the intermediate fractions, the operation might here be suspended, provided the pure products already obtained should be large enough for the purposes required.

But in my investigations, I have undertaken to prove the negative as well as the positive. I have attempted to carry the process of separation so far, that I might assert the absence of other bodies, as well as the presence of those obtained; and this clearing up of the intermediate fractions has generally been the most tedious part of the work. I have continued to operate upon these by themselves, until they also have become distributed in regular course — no new bodies appearing — among the fractions of constant boiling-point, or to such an extent that the intermediate quantities have become too small to admit of further continuance of the process.

This process has been in constant use in my laboratory during the last three years. In this time it has been applied in the study of petroleums, coal oils, the more volatile parts of coal- and wood-tars, the essential oil of cumin, commercial fusel oil, from corn whiskey, and even to mixtures more complex than either of these. As the result of this long experience, I can say that as regards bodies not decomposed by heat in distillation, I have not yet found a mixture so complex that it may not be resolved by this process into its proximate constituents so completely, that these shall have almost absolutely constant boiling-points. In repeated instances, even from petroleums, I have obtained these constituents so pure, that the contents of an ordinary tubulated retort charged with one of them has been completely distilled off without any essential change of temperature; i. e., not to the amount of $\frac{1}{2}°$ C., the thermometer frequently remaining absolutely constant for more than half an hour, a constancy of boiling-point not exceeded by that of distilled water. This state of purity, I think I may safely assert, has never before been attained from such mixtures by any system of fractional distillation.

As I shall soon be prepared to present to the Academy detailed results of the investigations above referred to, I may omit further allusion to them on this occasion.

I would remark, in conclusion, that it seems to me not improbable that this process may ultimately prove to be of great value in the arts. It is not too much to anticipate that, whenever the various constituents of the mixtures referred to shall have been separately and thoroughly studied in a pure state, some of them may be found to possess properties which will give to them great commercial value, sufficient to justify the expenditure necessary to separate them in large quantities.